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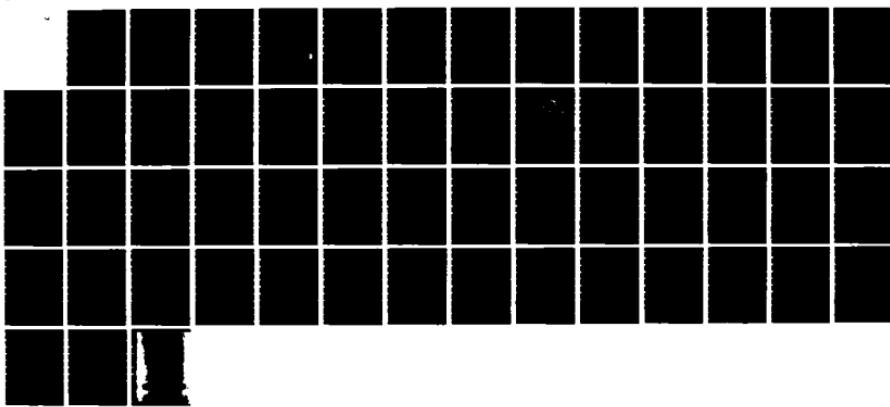
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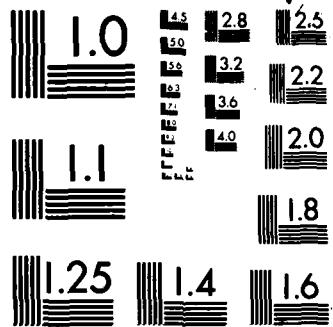
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NMAB-412	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) High-Performance, Low-Energy-Curing Resins		5. TYPE OF REPORT & PERIOD COVERED Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Committee on Room-Temperature Curing Resin Systems		8. CONTRACT OR GRANT NUMBER(s) MDA 903-82-C0434
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Materials Advisorv Board National Research Council 2101 Constitution Avenue, N.W. Washington, D.C. 20418		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE March 1984
		13. NUMBER OF PAGES 54
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Department of Defense National Aeronautics and Space Administration Washington, D.C.		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  This document has been approved for public release and sale; its distribution is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES  <b>S E L E C T E D</b> MAY 24 1984 <b>A</b>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Low-temperature cure                          Reactive solvents                          Fillers Advanced composites                          Waveguide curing Structural repair                            Epoxies Preordered reactions                        Secondary ring closing reactions Acrylate esters                              Donor acceptor complexes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Resin systems that are curable at reasonable rates at ambient temperature, or at slightly elevated temperatures, are needed for temporary repair of composite structures on damaged airframes. However, efforts to date have not been successful in yielding properties useful at temperatures higher than the cure temperature. The committee reviewed the state of the art and recommended a number of approaches for supported research. These include preordered reactions, acrylate esters, reactive solvents, waveguide curing, epoxy resins, secondary ring		

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HIGH-PERFORMANCE, LOW-ENERGY-CURING RESINS

Report of the Committee on  
Room-Temperature-Curing Resin Systems

NATIONAL MATERIALS ADVISORY BOARD  
Commission on Engineering and Technical Systems  
National Research Council



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Information	Classification
Approved	Confidential
Approved	Secret
Approved	Top Secret
Approved	Unclassified

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Date \_\_\_\_\_

Publication NMAB-412  
National Academy Press  
Washington, D.C.  
1984

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**NOTICE:** The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

The report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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This study by the National Materials Advisory Board was conducted under Contract No. MDA 903-82-C0434 with the Department of Defense and the National Aeronautics and Space Administration.

This report is for sale by the Defense Technical Information Center, Cameron Station, Alexandria, Virginia 22314.

Printed in the United States of America.

ABSTRACT

Resin systems that are curable at reasonable rates at ambient temperature, or at slightly elevated temperatures, are needed for temporary repair of composite structures on damaged airframes. However, efforts to date have not been successful in yielding properties useful at temperatures higher than the cure temperature. The committee reviewed the state of the art and recommended a number of approaches for supported research. These include preordered reactions, acrylate esters, reactive solvents, waveguide curing, epoxy resins, secondary ring closing reactions, donor-acceptor complexes, and the use of fillers, in conjunction with these approaches.

## PREFACE

The National Materials Advisory Board was asked by the Department of Defense (DOD) to study the problem of devising low-energy-curing (i.e., at room temperature or very slightly elevated temperatures) resin systems with elevated temperature properties. The objective of the study was to assess the state of the art and to recommend research endeavors most likely to lead to a resolution of the problem.

The major technical roadblock with systems investigated in the past is that the polymerization reaction does not proceed rapidly in the glassy state. The relationship between the temperature of cure and the glass transition temperature ( $T_g$ ) is described in the body of this report. It was not obvious how a material could be cured near room temperature with a use temperature acceptable for the application sought by the DOD--namely, a resin curable at a reasonable rate at ambient temperature capable of withstanding temperatures up to  $116^{\circ}\text{C}$  ( $240^{\circ}\text{F}$ ) and useful for the temporary repair of damaged airframes.

Because of the paucity of useful data in the literature, some exploratory studies were conducted by members of the committee to clarify the nature of the problem and to define new approaches. These studies were extremely useful in providing the committee with meaningful criteria to assess the earlier work in this area and to identify areas with potential opportunity.

The report consists of a chapter setting forth the sponsor's requirements and a background chapter summarizing the earlier studies devoted to the problem of room-temperature-curing resin systems. Fundamental interpretations are also provided in this latter chapter to explain the difficulties encountered by these earlier workers. The committee examined in some depth a number of alternate methods for addressing the problem, including novel curing techniques, preordered reactants, the role of fillers, rapid curing systems, and the possible development of low- $T_g$ , relatively high-modulus polymers. These methods are described in Chapter 5. Promising systems that merit possible DOD support are described further in Chapter 6.

Success in formulating a resin system that meets the requirements described in this report has greater implications than merely solving the problem at hand. A breakthrough could mean dispensing with energy-consuming autoclaves, could overcome the problem of built-in stresses due to differences in thermal coefficients of expansion between the fiber and organic matrix, and could possibly be used in a wider context--for example, for coatings and paints.

The chairman of the committee would like to thank all members of the committee for their time and effort spent in studying the problem and assembling the report. Thanks are also extended to the government liaison representatives for their participation and efforts. Special acknowledgment is given to Stanley Wentworth and Paul Hergenrother for their helpful technical contributions.

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## 1. INTRODUCTION

High-performance fiber-reinforced plastics are a new generation of versatile materials that provide significant increases in engineering design flexibility and manufacturing productivity. Among these advantages are reduced structural weight, improved corrosion resistance, increased fatigue resistance and reliability, and reduced manufacturing part count. These materials, termed "advanced composites" because of their high specific strength and modulus, represent an emerging technology that is revolutionizing the aircraft and missile industry. Already several military fighter aircraft are being manufactured with advanced composite materials accounting for nearly 20 percent of their structural weight. Business aircraft constructed of 80 to 90 percent advanced composite materials are in the flight-test stage--the last major test prior to receiving Federal Aviation Administration certification. All-composite helicopters are being designed, and new commercial aircraft are being delivered containing as much as 1540 kg (3400 lb) of advanced composite materials. Military and civilian aircraft in the future will be designed to take even greater advantage of the performance benefits provided by advanced composites. By the end of this century, it is predicted that most of the structural components of military aircraft and helicopters and perhaps half of the structure of civilian transports will be fabricated of advanced composite materials. With the advent of reinforced plastics into such demanding structural applications, it can truly be said that the era of plastics has arrived.

The increased use of advanced composites as structural materials has identified several new technical areas requiring additional development. For example, improved plastics possessing greater toughness are needed to increase damage resistance and damage tolerance; processable, thermally stable resins for elevated-temperature applications are desired; low-energy-curing resins would further reduce manufacturing costs; and environmentally stable resins are sought for a variety of exotic operating conditions and applications ranging from the outer reaches of space to automobile engines.

One of the more acute needs is for resins suitable for use in making structural repairs. Commercial "superglues" are acceptable for household use, but resin systems that are highly sophisticated formulations, designed especially for structural repair are needed. Resins have to be developed that are capable of being cured at temperatures significantly lower than those commonly employed in the manufacturing process but providing mechanical properties comparable to those of the original resin of manufacture. Studies of resins commercially available in the industry and several research efforts aimed specifically at developing new

low-temperature or low-energy-curing resins have failed to yield suitable products. With so many applications already committed to production and several new uses in the formative stages, the need for a practicable repair technology is here. The engineering requirements for structural repairs are well understood. What is needed is an innovation in resin-curing technology.

#### STATEMENT OF THE PROBLEM

Perhaps no machine is required to perform more functions on a routine basis, day in and day out, than a modern jet aircraft. The military operator demands and expects the utmost in performance in terms of speed, maneuverability, range, and payload. Although not flown nearly as often as a civilian transport, military aircraft must be maintained in a state of readiness at all times. In fact, the ability of the aircraft to perform its mission or to be maintained in a state of readiness may well determine the outcome in times of conflict. Rapid repair technologies are required to assure mission performance and to maintain combat readiness.

In the civilian sector, operating economies demand efficient, highly reliable aircraft. Often civilian aircraft are flown 8 to 12 hours per day or more. The need to maximize aircraft utilization requires rapid, efficient repair technologies to minimize aircraft "out-of-service" time or the need for replacement parts. Both the military and civilian sectors have well-developed repair technologies for conventional aircraft structures. The advent of advanced composite structures, however, requires new repair methodologies.

Advanced composite structures are composed of continuous filaments of high-strength fibers, usually graphite or boron, embedded in a polymeric matrix. The polymer matrix determines several of the useful limits of the composite. For example, the sensitivity of Tg to water absorbed from the environment may determine the maximum speed of a supersonic aircraft. In the repair of damaged advanced composite structures, it is usually necessary to return the structure to its original state of mechanical performance, or nearly so. Even when the repair is fabricated from the original materials and processes of manufacture, this can pose a formidable challenge because of the temperatures and pressures involved. Future utilization of advanced composites will require an ability to perform the repair in a battle zone, forward base, or at a civilian operator's "line station," away from the processing facilities maintained at a major overhaul or repair base. Entwined in this requirement is the need for repair materials and processes that are fast yet simple, require a minimum of processing facilities, and can be implemented at low, preferably ambient, temperatures.

Aircraft structures are damaged most often from routine ground-service incidents, such as striking a parking ramp or being struck by a ground-service vehicle. Other causes include in-flight impacts with birds, hail, etc. Military aircraft are also subject to battle damage. If the damage is minor, such as a simple puncture, or if the structure is

"designed to be repaired," simple hole-filling may be all that is required. More extensive damage or more complex, sophisticated structures require removal and replacement of the damaged composite material.

Current composite repairs are of two types: the adhesive-bonded repair and the cocured repair. In the adhesive bonded repair, metal or a precured composite laminate is adhesively bonded to the structure to effect the repair. Advantages of this technique for repair include known quality of the structural replacement member and the simplicity of adhesive-bonding repairs. In this instance the repair resin of concern is that utilized to formulate the adhesive. The patch material is either metal or a composite prefabricated at a manufacturing facility. The disadvantage of this type of repair is the availability, especially at forward stations, of repair patches of the proper thickness, dimension, contour, and fiber orientation.

In the cocured repair, reinforcing fibers and uncured resin are located on the structure and then cured and adhesively bonded to the existing structure in a single operation. The advantages of this type of repair are ease of preparation, ability to tailor to existing contours, and ability to tailor the repair for the specific damage. Disadvantages include the need for storage of thermally unstable materials (often refrigeration is required) and the need for local sources of heat and pressure.

Both adhesive-bonded and cocured repairs call for the use of resin materials to effect repair. The resins must be stable under ambient storage conditions, be nontoxic, be solvent-free (or at least must not evolve significant gaseous by-products during cure), have a low shrinkage upon cure, and be capable of wetting and adhering to other composites and metals common in aircraft construction. Several key mechanical properties for the two resin systems are different although not necessarily mutually exclusive (see Chapter 3). Cocured resins must also be of low viscosity in order to penetrate and wet the fiber bundles. Adhesive repair resins will be formulated to relatively high viscosities to ensure a minimum bondline thickness and to fill gaps and minimize adhesive "squeeze out."

A review of the commercially available resins and examination of the results of several directed development efforts found no resins that meet these criteria. The inability of existing materials to maintain stiffness (in terms of shear modulus) and/or strength at temperatures much above the cure temperature is the greatest single factor limiting low-energy, low-temperature structural composite repairs.

#### OBJECTIVES

The objectives of this effort are to perform a scientific assessment of the state of the art in pertinent areas of polymer science in order to develop new approaches using existing technology or to indicate the new technology needed to find acceptable solutions to the problem, and to establish priorities.

## 2. SUMMARY

The general conclusions of the committee are summarized as follows:

- o There is a critical need for a low-energy, rapid-curing matrix/adhesive for structural repair in the field for military airframes.
- o Despite past DOD funding, to date no system has been developed with the desired features--namely, retention of good thermomechanical properties up to 116°C (240°F) obtained by curing in bulk at room temperature. No work is currently being funded in this area primarily because of the absence of any approaches with some chance of success.
- o The major technical roadblock in systems investigated in the past is that the polymerization reaction does not proceed rapidly in the glassy state. Consequently, it was not obvious as to how one could cure a material near room temperature and yet achieve a cured resin with a use temperature of 116°C (240°F).
- o Even if one were successful in designing a system with the features described, formidable problems would still remain because the material would have to cure without giving off volatiles, and the cured resin should have the requisite thermomechanical properties and be relatively insensitive to moisture.
- o Isolated examples in the literature were identified by the committee that suggest that unique solutions to the problem may exist.

The committee specifically concluded that

- o There are several approaches that separately or in combination may provide the improvements to achieve the stated goal. These approaches include use of more reactive epoxies and vinyls, improved catalysts, and the possible incorporation of fillers.
- o Use of preordered reactants may provide a unique solution to the problem.

- o Achievement of systems with acceptable modulus and low Tg for use as an adhesive to attach preformed, precured composites provides a much higher probability of success with the various techniques considered and permits inclusion of other methods such as reactive solvents.

Finally, the committee has identified novel systems and curing techniques from this study that may be pertinent to the current problem but, in addition, could have far broader implications for polymer technology.

### 3. REQUIREMENTS

There are three levels of repair that can be considered for airframes and airframe components. These are, first, at the factory or maintenance depot, where components may be completely or nearly completely rebuilt or reworked; second, at the base, where structural repairs are limited to certain maximum sizes and locations on the aircraft; and, third, in the field, where rapid turnaround of the aircraft is of utmost importance and where only portable equipment and repair kits can be presumed to be available. In the case of field repair facilities, the environmental conditions under which the repairs may be made are under a minimum of control, and temperatures may be presumed to be in the range of 5 to 50°C (41 to 122°F), depending on the geographic location. Power to run small hand tools, small heating blankets, lights, and air compressors may be available; however, power to run high-wattage equipment such as ovens and large heating blankets normally would not be available, especially during wartime. Field repairs are not intended to be the permanent, highly sophisticated repair that can be performed at the factory, depot, or rear base. They must, however, return the structure to full flight status for an undetermined period. If this cannot be accomplished in a timely manner and if a replacement part is not available to allow completing the military mission, the airframe is set aside and used for spare parts. In commercial situations, replacement aircraft may be required at the penalty of high costs and potential losses in revenue.

There are three types of structural repairs that may be considered--namely, mechanically fastened, adhesive-bonded, and cocured.

Mechanically fastened repairs to composite structures have been the subject of considerable study by the Navy. Although promising from some aspects, the techniques developed rely on preformed metallic details that may or may not be available when needed in forward base areas.

The technology of adhesive-bonded repairs to metal airframe components has been well studied, and highly developed procedures have been evolved for both the factory or depot and base areas. However, the bonded structural repair of both metal and composite components under field conditions is seriously constrained because of the lack of adequately performing room-temperature (low-energy) curing adhesives and matrix resins. The Air Force and the Navy made several attempts to develop such materials via the formulation route without notable success. The requirements for such materials are driven by the turnaround times dictated by sortie generation studies and by the structural repair design analysis.

The need for rapid turnaround dictates resin systems that cure in short times. The lack of facilities at forward field locations prescribes the need for low-temperature--i.e., ambient-temperature--curing. The challenge is to develop such resin systems that also possess the mechanical strength and modulus necessary to restore the structure to an acceptable level. The potential approaches for developing such resins are the goals of this report.

Adhesive-bonded composite repairs are of two types: the bonded, precured patch and the wet lay-up, cocured patch. In the former a precured composite or metal plate is adhesively bonded to the structure to form the repair. The repair resin in this case is the adhesive. Structural requirements dictate that such adhesive bonds provide at least 7 MPa (1000 psi) in the hot/wet lap shear at 116°C (240°F). The adhesive shear modulus requirement is estimated to be 0.3 GPa (50,000 psi) minimum under the same conditions. In the wet lay-up repair, the "wet" resin and reinforcing fabric are combined and located on the structure. Curing in place occurs, and the resin serves as both the matrix for the composite repair and the adhesive for the repair. The matrix requirements for this application are more stringent than those for an adhesive alone. Specifically, a matrix tensile modulus of 1.7 GPa (250,000 psi) in the wet condition at 116°C (240°F) is the goal. In both cases, the resins are required to cure in 1-4 hours at temperatures less than 25-47°C (77-117°F); that is, at temperatures less than 10-20°C (18-36°F) above presumed ambient conditions of 16-27°C (60-80°F).

A minor increase in cure temperature may be permissible at some locations. The materials preferably should be a single component but it appears that a two-component system that can be easily mixed may be necessary. Completely solvent-free systems are desired. Innovative packaging approaches may be required for the latter. Adhesives and resins should be nontoxic or of a low order of toxicity and be storable in the temperature range of 4 to 49°C (40 to 120°F) for a minimum of 1 year. The materials should cure properly under conditions of high humidity and not require optimum surface preparation of both metal and composite surfaces. Once cured, resistance to fuel and lubricants is a requirement.

The temperature requirement of 116°C (240°F) derives from possible aerodynamic heating that occurs on present-day fighter aircraft. This requirement may be significantly higher with future military aircraft. While the effects of temperature must be resisted by the polymer matrices and adhesives utilized in repair, aerodynamic heating cannot be relied on to assist or augment the curing of the polymers. For example, the process of aerodynamic heating may occur at a rate as high as 30°C/minute (54°F/minute). However, it should be noted that modeling of the temperature profiles through the thickness is very difficult, and only rough estimates are currently available.

The durability of these materials must be such that the repaired structures will have a service life of 100 flight hours during a 30-day period.

To summarize, the key features that must be designed into this resin include the following:

- o Ability to cure in 1-4 hours at temperatures less than 25-47°C (77-117°F) to obtain a structural resin with a use temperature of 116°C (240°F).
- o Wet tensile modulus of 1.7 GPa (250,000 psi) at 116°C (240°F).
- o Prepolymer (no solvent) that wets the lay-up and cures without evolving gases.
- o Nontoxic and storable from 4 to 49°C (40 to 120°F) for one year.

While the principal goal of this study is field-level repair, it is likely that materials developed for this purpose would find application for repairs at the base and depot as well as for primary fabrication at the factory.

#### 4. BACKGROUND

In this chapter the classical limitations on  $T_g$  with respect to curing temperature ( $T_{cure}$ ) are discussed in terms of the time-temperature-transformation (TTT) diagram of Gillham (1982). Then various resin systems are categorized with respect to observed deviations between  $T_g$  and  $T_{cure}$ . Finally, earlier work carried out to develop either low- or intermediate-energy-curing resins is reviewed.

##### FUNDAMENTAL LIMITATIONS

The general problems and limitations associated with producing an ambient-temperature-curing adhesive or matrix that maintains glassy behavior above its cure temperature requires an understanding of the overall curing process of thermosetting resins. A TTT diagram (analogous to the TTT diagrams that have been employed for many years in metallurgical processing) may be used to provide an intellectual framework for understanding and comparing the cure and physical properties of thermosetting systems (Gillham 1982; Enns and Gillham 1983a,b; Naé and Gillham 1983).

The isothermal TTT diagram (Figure 1) is obtained from measurements of the time to gelation, vitrification, and devitrification versus temperature. The influence of the gelation, vitrification, and devitrification on chemical and mechanical properties is immediately obvious from a scrutiny of the TTT diagrams. Specifically, gelation limits the macroscopic flow and limits aggregation of a dispersed phase (as in rubber-modified systems); vitrification limits further chemical reaction. Other important considerations include the following:

- o Isothermal cure at a given temperature ( $T_{cure}$ ) below  $T_{g\infty}$  will (in principle) lead to  $T_g = T_{cure}$ . The relationship between  $T_g$  and  $T_{cure}$  is discussed in the next section.
- o Complete cure is obtained (in principle) only by curing above  $T_{g\infty}$ .
- o The limiting viscosity in the fluid state is controlled by gelation above  $gelT_g$ , and by vitrification below. At gelation the weight-average molecular weight and zero shear rate viscosity become infinite. Viscosity in the vicinity of vitrification is generally described by the Williams-Landel-Ferry (WLF) equation (Williams et al. 1955). Isothermal reactions proceed only slowly after vitrification. Below  $gelT_g$  this can lead eventually to gelation. Shrinkage stresses develop by additional cross-linking after gelation.

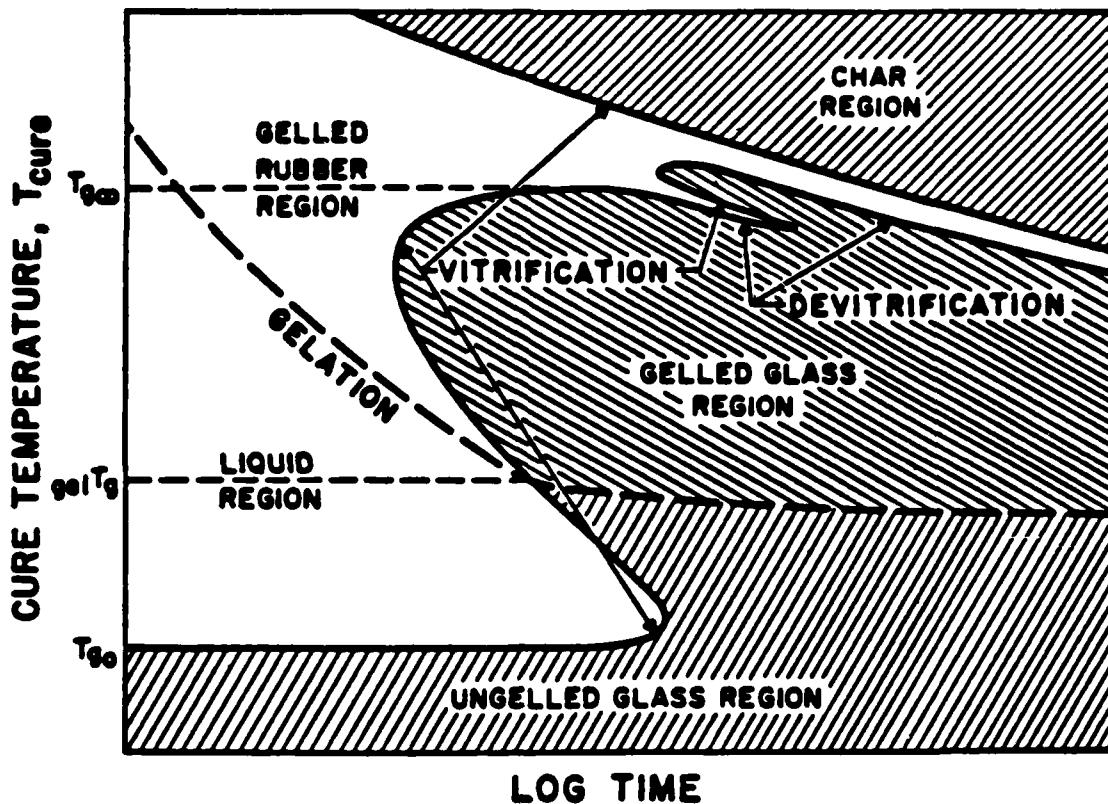


FIGURE 1 Isothermal time-temperature-transformation (TTT) diagram of a thermosetting polymer showing three critical temperatures ( $T_{g\infty}$ ,  $gelT_g$ , and  $T_{g_0}$ ) and four distinct states of matter (liquid, gelled rubber, gelled glass, and ungelled glass) that pertain to cure.  $T_{g\infty}$  is the maximum glass transition temperature of the cured material;  $gelT_g$  is the temperature at which the times to gelation and to vitrification are equal;  $T_{g_0}$  is the glass transition temperature of the reactants. At high temperatures thermal degradation can lead to vitrification and devitrification, depending on whether the glass transition temperature increases from the rubbery to the glassy state or decreases from the glassy to the rubbery state.

- o The limitations imposed on achieving a  $T_g$  well above  $T_{cure}$  suggest that the resin might be stiffened above  $T_{cure}$  by the addition of a rigid dispersed phase. Thus, incorporation of a filler can enhance the bulk viscosity before cure and the modulus after cure. The upper application or use temperature will be somewhat extended, although some ultimate properties may be decreased. Similarly, if the matrix or an added second component can crystallize, it will enhance the stiffness and some related mechanical properties.

- o The morphology developed in a two-phase system (e.g., those in which rubber-rich domains precipitate as a dispersed phase from an initially homogeneous solution) on isothermal cure depends on the gelation temperature. The reaction temperature determines the competition between thermodynamic and kinetic (transport) factors. For optimum mechanical properties, a two-phase system will be cured at one temperature to control the morphology and subsequently cured above  $Tg_{\infty}$  to complete the reactions of the matrix.
- o The times to gelation and vitrification can each be computed from the reaction mechanism and kinetics and the conversion at gelation (which is constant, according to Flory's (1953) theory of gelation) and the conversion at vitrification, respectively. Since vitrification occurs when the  $Tg$  rises to  $T_{cure}$ , computation of the time to vitrify involves knowledge of the relationship between  $Tg$  and conversion. Comparison of experimental and fitted data of the times to gelation and to vitrification for one epoxy system suggests that diffusion affects reaction rate only in the vicinity of vitrification (Enns and Gillham 1983b).
- o The vitrification curve is S-shaped for both linear and network-forming step-growth reactions and for linear chain growth reactions (Aronhime and Gillham 1983). At temperatures immediately above  $Tg_0$  the time to vitrification passes through a maximum whereas just below  $Tg_{\infty}$  the time to vitrification passes through a minimum. The minimum is the consequence of an interplay between the increasing reaction rate constant and the decreasing concentration of reactants at vitrification with increasing temperature. The maximum is the consequence of an interplay between the decreasing physical viscosity and the effect of increasing reaction rate constant (in increasing viscosity through increasing molecular weight) with increasing temperature.
- o The fractional extent of reaction at vitrification and the time to vitrify, like gelation, decrease with increasing functionality (Naé and Gillham 1983).
- o The rate of increase of  $Tg$  with conversion increases with conversion (Enns and Gillham 1983b).
- o The reaction mechanism of a particular thermosetting system in principle can be deduced from the shape of the experimentally measured S-shaped vitrification curve.

A point in relation to the use of glassy polymers as matrices and adhesives is their tendency to age--i.e., display some degree of time-dependent character. Thus one finds that modulus usually increases linearly with the logarithm of time while some ultimate properties and transport properties decrease. The further the temperature is below  $Tg$ , the slower is the rate of change for a given glassy polymer. This time-dependent behavior is caused by the nonequilibrium character of the

glass produced by a finite cooling rate from the liquidus (rubbery) state into the glass state and is generally referred to as "physical aging." The time-dependent behavior is a result of the system's approach to equilibrium. This typically results in a time-dependent densification, which in turn lengthens segmental relaxation times. It is interesting to note that the modulus and density in the glassy state at a given temperature can decrease, whereas absorption of water can increase with increasing extent of cure (Enns and Gillham 1983a,b). This apparently anomalous behavior is also a consequence of the nonequilibrium nature of the glassy state: the higher the  $T_g$ , the longer are the relaxation times and the further from equilibrium are the room-temperature properties. In summary, nonequilibrium behavior, characteristic of the glassy state, can influence long-term properties and thus the eventual selection of a candidate resin.

#### THE RELATIONSHIP BETWEEN $T_g$ AND $T_{cure}$

The objective of this section is to compare the  $T_g$  of a material after prolonged isothermal cure with the value of  $T_{cure}$ . In the previous section it was stated that isothermal cure at temperatures below  $T_g$  will (in principle) lead to  $T_g = T_{cure}$ . This would be a valid statement if the chemical reactions were quenched at vitrification, which was defined to occur when the  $T_g$  rose to  $T_{cure}$ . In practice the usual methods that measure  $T_g$  do not lead to this equivalence. The  $T_g$  is usually measured to be higher than the  $T_{cure}$ . Nevertheless  $T_g$  is determined by  $T_{cure}$ .

The transformation of the amorphous glassy state to the rubbery state by heating is designated the glass transition. Although it usually occurs over a temperature range of about  $80^\circ\text{C}$  ( $144^\circ\text{F}$ ), it is commonly measured by a representative single temperature that is midway between the limiting states. For example, it may be measured by the inflection in the curve for modulus versus temperature, or by a peak in the curve for dynamic mechanical loss versus temperature. It is reproducible from laboratory to laboratory when the heating rate as well as the method is defined. Thus the  $T_g$  of high-molecular-weight polystyrene is reported to be  $100^\circ\text{C}$  ( $212^\circ\text{F}$ ) at 1 Hz from the location of the local maximum in the dynamic mechanical loss modulus at a rate of heating (or cooling) of  $1^\circ\text{C}/\text{minute}$  ( $1.8^\circ\text{F}/\text{minute}$ ). The local motions at this temperature are intermediate between the highly restricted motions characteristic of the glassy state and the relatively unrestrained, submolecular cooperative motions characteristic of the rubbery state. Chemical reactivity depends on the degree of molecular mobility and thus on the physical state of the material. For typical epoxies in the fluid or rubbery state, the reactions are "kinetically" controlled; in the vicinity of  $T_g$  (as usually defined, such as above) they are "diffusion" controlled, whereas well into the glassy state they are "quenched". It therefore follows that if  $T_g$  is measured in a usual way (as above), then as isothermal polymerization proceeds,  $T_g$  will rise through the  $T_{cure}$  approaching a limit that corresponds to highly restricted local motions. Since the  $T_g$  region for many epoxy systems is about  $80^\circ\text{C}$  ( $144^\circ\text{F}$ ) in width, in practice the limiting  $T_g$  is about  $40^\circ\text{C}$  ( $72^\circ\text{F}$ ) above the temperature of isothermal cure. An example of  $T_g$  versus  $T_{cure}$  is shown in Figure 2 (Schneider and Gillham 1980).

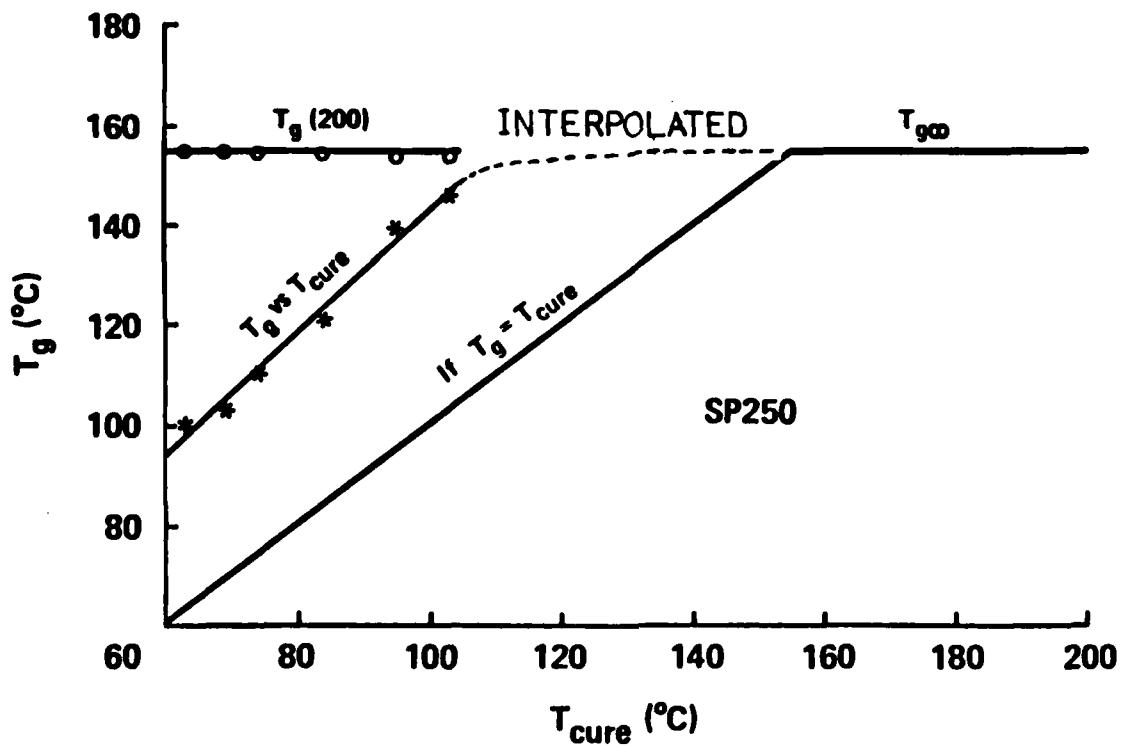


FIGURE 2:  $T_g$  versus  $T_{\text{cure}}$ . Specimens were cured isothermally at  $T_{\text{cure}}$  for prolonged times before measuring  $T_g$  (Schneider and Gillham 1980). The maximum  $T_g$  [ $T_{g\infty} = 156^\circ\text{C}$  ( $313^\circ\text{F}$ )] was measured on cooling at  $1.5^\circ\text{C}/\text{min}$  ( $2.7^\circ\text{F}/\text{min}$ ) after heating to  $200^\circ\text{C}$  ( $392^\circ\text{F}$ ). Note  $T_g \geq T_{\text{cure}} + 40^\circ\text{C}$  ( $72^\circ\text{F}$ ) to  $T_{\text{cure}} < \text{approx. } T_{g\infty} - 50^\circ\text{C}$  ( $90^\circ\text{F}$ ).

The discussion to this point on the relationship between  $T_g$  and  $T_{\text{cure}}$ , obtained after vitrification and chemical quenching during isothermal cure, has assumed that the value of  $T_g$  does not change during measurement. The  $T_g$  will increase during the temperature scan to an extent that depends on the reactivity of the system in this temperature range. The reactivity in turn will be determined by the intrinsic kinetic rate constants for the reaction and the residual concentration of reactive sites at vitrification. Examples of these factors follow. The rate constant for the cure of an epoxy with an aliphatic amine is generally higher than with an aromatic amine. The residual concentration of reactive species at vitrification can be increased by increasing the functionality of the reactants. (In epoxies the number of functional groups is usually two, but can be higher. The epoxy equivalent weight usually decreases as functionality increases.) A study (Naé and Gillham 1983) has shown an increase in  $T_g - T_{\text{cure}}$  with increasing functionality.

of the cross-linking agent. The increased residual concentration of reactive sites at vitrification arises partly from the higher concentration of reactive sites in the reactants but mainly from the lower chemical conversion at vitrification for the more highly functional systems.

The conclusions of this section, which concerns the isothermal cure below  $Tg_{\infty}$  of a homogeneous system, as to quenching of the chemical reactions are as follows:

Case I.  $Tg = T_{cure}$  if the definitions of  $Tg$  and vitrification are consistent.

Case II. In general, for many epoxy systems  $Tg \approx T_{cure} + 40^{\circ}\text{C}$  ( $72^{\circ}\text{F}$ ) because the usual way for defining  $Tg$  places it midway between the glassy and rubbery states.

Case III.  $Tg > T_{cure} + 40^{\circ}\text{C}$  for systems with increasing functionality.

The value of  $Tg - T_{cure}$  in principle can be increased by having the reactions proceed further in the vitrified state than epoxy reactions (Gillham 1983). This should be facilitated by close proximity of reaction sites as in the polyamic acid precursors to polyimides, and for ordered side groups (see Chapter 5, section on preordered reactions.)

#### EARLIER STUDIES

In this section earlier studies aimed at developing low-temperature-curing, high- $Tg$  resins are reviewed. Discussions of a number of DOD-funded programs and also of work aimed at achieving ultra-high  $Tgs$  by curing at intermediate temperatures are included. The status of room-temperature-curing resins in industry is also summarized.

##### Work on Low-Energy-Curing Resins

Efforts to develop high-performance polymer systems curable at room temperature for use as matrix resins and in adhesive formulations have been the subject of contractual study programs sponsored by both the Air Force (Delano et al. 1978) and the Navy (Crabtree 1979; Crabtree 1981; and Brenner and Arnon 1981). None of these efforts produced resin systems that would fully meet the requirements established herein. However, the results of this work suggest that a modest potential exists to meet these criteria with both epoxies and acrylate esters.

The Navy efforts concentrated on adhesive formulations. Since electric power is always available on carriers, cures up to  $121^{\circ}\text{C}$  ( $250^{\circ}\text{F}$ ) by using heating blankets were considered acceptable. Thus, by definition, the requirements were not the same as those set forth in this study. The important contribution from this effort was that high-temperature bond strengths [ $> 9.65 \text{ MPa}$  at  $121^{\circ}\text{C}$  ( $> 1400 \text{ psi}$  at  $250^{\circ}\text{F}$ )] could be obtained by using high-functionality resins. Formulations based on a cresol novolac epoxy (Ciba Geigy ECN-1299), the triglycidyl ether of p-aminophenol (Ciba-Geigy 0510), and tetraglycidylmethylenedianiline

(Ciba-Geigy MY-720) all performed well even when heat-cured with aliphatic amines. This work also indicated a potential for the acrylate esters, frequently referred to in the trade as vinyl esters. A follow-up effort demonstrated that cycloaliphatic amine curing agents such as bis(4-aminocyclohexyl)methane (PACM-20) offered advantages over the aliphatic amines in elevated-temperature performance. This latter effort further demonstrated that toughening the resin system by prereaction with carboxy-terminated butadiene-acrylonitrile elastomers gave improved bond strengths and moisture resistance. However, none of the resin systems completely fulfilled the requirements set forth in this report.

The Air Force approach was aimed at both laminating resins and structural adhesives. A survey indicated that no suitable room-temperature-curing adhesives were available. The general conclusions were that isocyanate-based systems were unsuitable for field repair because of poor shelf stability (moisture sensitivity), that vinyl esters may lack moisture and heat resistance, and that elevated temperatures would be required to achieve 116°C (240°F) performance. The most promising resin system evaluated was formulated from an epoxy novolac (Dow DEN438) cured with a cycloaliphatic amine (isophoronediamine). Here again, none of the systems met the requirements described herein.

The unavailability of commercial materials that meet the requirements of this study is further demonstrated by the modulus temperature data shown in Figure 3. This was an investigation conducted by a major commercial aircraft manufacturer on commercially available room-temperature-curing adhesives. The moduli of all the products evaluated decline rapidly at temperatures in excess of 38°C (100°F.) Note, however, that one of these products shows a modulus response in the 120-150°C (250-300°F) range. The manufacturer claims that this glass-filled product has useful properties near 150°C (300°F). It could thus be concluded that this observation is the result of additional cure upon heating to the test temperature.

The data presented in Figure 3 on the Hysol 934 glass-filled resin prompted the committee to explore in more detail the effect of fillers on the properties of resins. A considerable amount of work exists in the literature on this subject. For example, very fine carbon particles exercise a dramatic effect on the dynamic modulus of natural rubber. With respect to glasses, it is well known that the addition of rigid fillers results in an increase in the heat deflection temperature. Even though room-temperature-curing places limits on the Tg that can be achieved because of the onset of vitrification, glasses that are reinforced with an appropriate filler usually display a higher thermal limit on the critical value of modulus due to the enhanced stiffness.

This behavior is seen in Figure 3, where plots of the storage modulus, G', versus temperature are shown for several unfilled resins along with one such resin that had been reinforced with a rigid glass filler. It is clear not only that the reinforced system displays a higher modulus over the entire range of temperatures but also that the temperature at which the modulus drops to the order of 0.6 GPa (100,000 psi) is distinctly higher than those of the unreinforced resins.

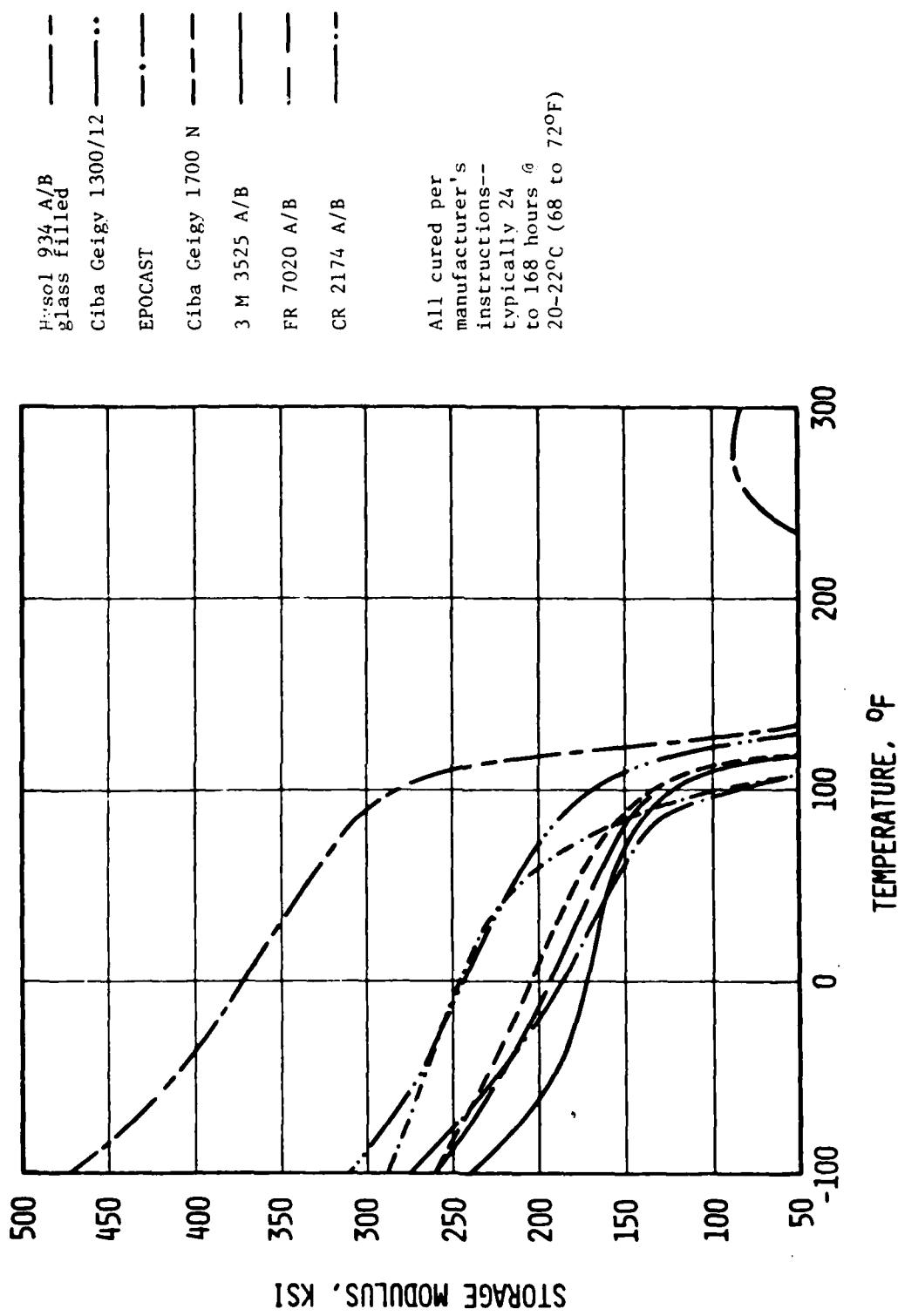


FIGURE 3 Shear modulus-temperature behavior of several commercial room-temperature-cured resins. Source: J. Quinlivan, private communication.

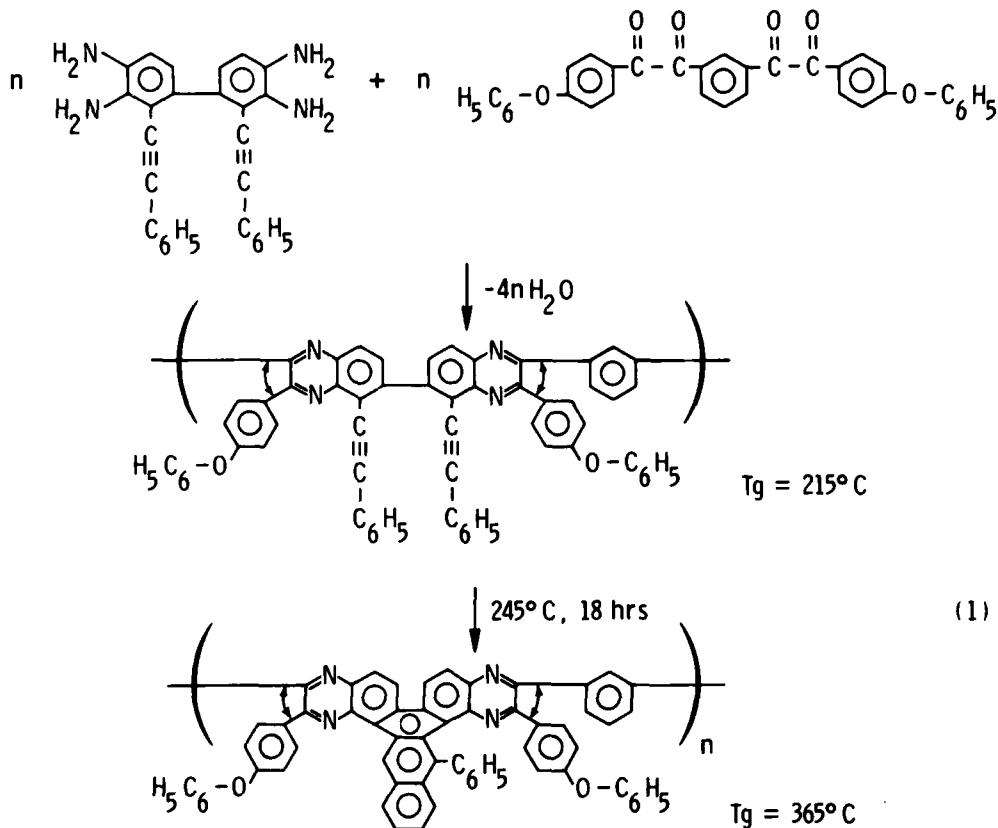
There may be a number of concerns on utilizing fillers; some of these are as follows:

- o Increase in viscosity of the unfilled, uncured resin through addition of filler, its dependence on filler content, and effects on processing.
- o Relative effect on reaction kinetics of the unfilled resin by the presence of a filler.
- o Degree of "wet out" of the filler and its correlation with mechanical enhancement.
- o Potential need of coupling agents for enhancing the matrix-filler compatibility.
- o Effect of specific surface of the filler on viscosity and related solid-state mechanical properties.
- o Relative trade-off between stiffness and impact properties by addition of a rigid filler.
- o Influence of the particle size and shape of the filler--e.g., rods, spheres, or flakes.
- o Possible potential stress concentration problems caused by differences in thermal expansion coefficients between filler and matrix.
- o Potential enhancement of moisture adsorption within the adhesive layer caused by the nature of the filler.

#### Work on Intermediate-Energy-Cured Systems

The concept of reacting pendant or side chain groups on a polymer to increase the Tg has also been explored. Either intramolecular or intermolecular reactions can occur, depending on the nature and location of these groups. Intermolecular reactions are the more limiting because of the difficulties in properly aligning the reacting groups once the polymer begins to gel or vitrify. There are reports of intramolecular reactions in the literature; however, to meet the DOD requirements successfully, the bulk state reaction(s) must occur without the evolution of volatiles.

In an attempt to address the processing problems prevalent in using high-temperature polymers, the intramolecular cycloaddition concept was investigated at the Air Force Wright Aeronautical Laboratory. This work, directed toward attainment of high-Tg polymers, served as a useful means for evaluating various approaches. One approach was based on a model compound reaction (White and Sieber 1967) in which 2,2'-bis(phenylethynyl)biphenyl was thermally converted to 9-phenyl-dibenz[a,c]anthracene in high yields (~80 percent). A polyphenylquinoxaline containing 2,2'-bis(phenylethynyl)biphenyl moieties in the repeat unit was prepared (Hedberg and Arnold 1976):



After curing at 245°C (473°F), the Tg was 365°C (689°F) (possible further curing occurred during the Tg measurement). Regardless of whether this was the result of glassy state cure or the method of Tg determination, the result is encouraging.

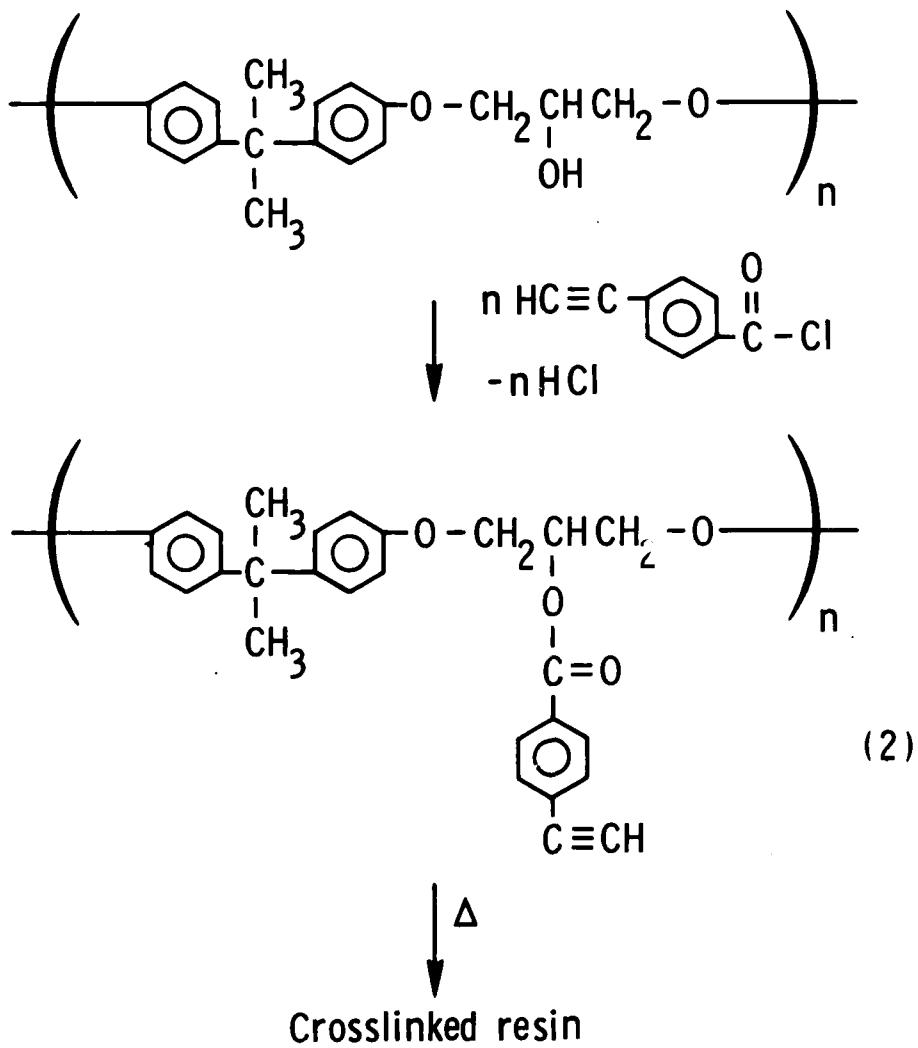
It should be noted, however, that the earlier work of White and Sieber was carried out in dilute solution, a condition that would favor intramolecular cyclization. When a similar study with model compounds was carried out by Hedberg and Arnold, it was found that intermolecular addition proceeded at twice the rate of the intramolecular condensation. Hence, the results in curing the polymer were achieved primarily through intermolecular rather than intramolecular condensation.

Another alternate route to an intramolecular cycloaddition involved an enyne ( $-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-$ ) group within a polysulfone (not pendant) (Reinhardt 1981). The enyne group could theoretically cyclize to a rigid naphthalene moiety. However, intermolecular reactions of the vinyl groups occurred, causing cross-linking.

There are many examples of intermolecular reactions of pendant groups on polymers that lead to branching and cross-linking. A polybutadiene-amide-imide from the reaction of the diacid chloride of Hystil C-1000 (a carboxylic acid-terminated 1,2-butadiene oligomer with number-average molecular weight of 1350 g/mole) with an aromatic amide-imide diamine was thermally cross-linked through the pendant vinyl groups in the polybutadiene segment (Jablonski 1970). Work on high-temperature

polyphenylquinoxalines again served as a useful guide to intermolecular cross-linking reactions. Cyano, cyanato (Hergenrother 1974), active methyl (Wentworth 1977), ethynyl, and phenylethyynyl (Hergenrother 1981) groups have been incorporated pendant on polyphenylquinoxalines and thermally reacted to increase the Tg. In all cases, the Tg is governed by the final T<sub>cure</sub> until Tg<sub>∞</sub> is attained.

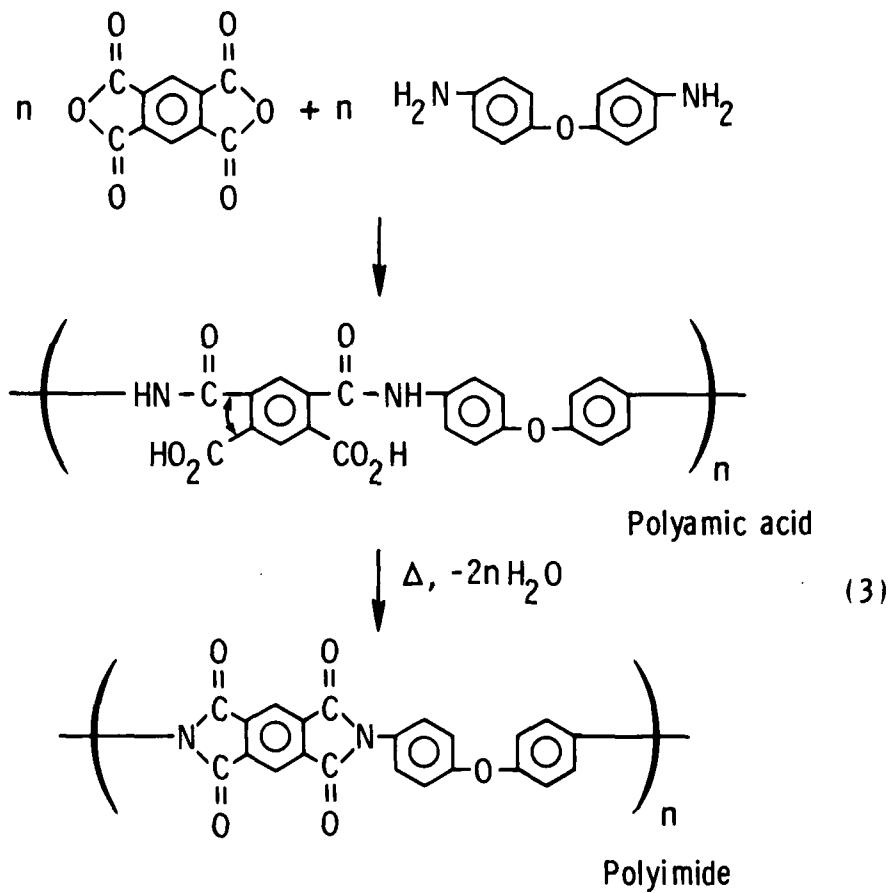
To verify earlier findings, an attempt was made by a member of the committee to determine if a polymer containing a high concentration of reactive pendant groups could be cured without volatile evolution and give a Tg significantly higher than T<sub>cure</sub>. The pendant hydroxy groups of a phenoxy resin ( $M_n = 24,000$  g/mole) were reacted with 4-ethynylbenzoyl chloride to place a pendant ethynyl group on each repeat unit:



As determined by torsional braid analysis [TBA, heating rate of 3°C/min (5.4°F/min)], the initial Tg of the polymer was 89°C (190°F). It was raised to 210°C (410°F) after 2 hours' heating in nitrogen at 200°C (392°F); 238°C (460°F) after 2 hours at 200°C (392°F) in air; and 240°C (464°F) attained after 2 hours at 300°C (572°F) in air. Again some curing may have occurred during the TBA measurements. However, the same conclusion was reached as with most of the earlier work; the Tg for intermolecular reactive polymers is governed by the final Tcure.

### Curing of Polyimides

Polyimides are perhaps the best illustrative example of a very high Tg polymer resulting from a lower temperature cure. Thus, thermal curing of a thin film (2-5μm) of polyamic acid based on pyromellitic anhydride and 4,4'-oxydianiline at 150-175°C (302-347°F) produced a polyimide with a Tg in excess of 385°C (725°F) (J. Economy, private communication):



Interestingly, in the presence of pyridine and trifluoroacetic anhydride, the cyclization tended to take a different course, yielding isoimides as the primary product. Clearly chain conformation plays a critical role in determining the kind of intramolecular condensations that can occur or, as noted earlier, intermolecular reactions.

## 5. APPROACHES

### HOT REACTIONS

The term "hot reaction" refers to resin systems that react with sufficient rate to yield products with useful strengths during external heating. Typically, such reactions may be accompanied by large exotherms that potentially could provide an additional boost to the curing process. Even though the resin may not be fully cured, further reaction during external heating could proceed at a rate that assures that the material maintains high modulus up to its maximum-use temperature, which in this case is defined as 116°C (240°F). However, exothermic curing or aerodynamic heating cannot be relied on for final cure. Hence, the systems and approaches described in this section, although incorporating important advantages over earlier work, must be looked on as incremental solutions to the problem.

This is best understood by considering the time-temperature-transformation cure diagram (Gillham 1982). Once a matrix material cures to the glassy state at a given  $T_{cure}$  there is a minimum allowable time for heating to the maximum-use temperature. Any external heating that exceeds this rate may cause the modulus and strength to drop too low and cause structural failure. As noted earlier, the greatest opportunity for achieving the incremental increase in  $T_g$  is through the use of Case III-type resins that continue to react during the temperature scan, leading to increased values of  $T_g$  during this period. This effect is strongly enhanced with increases in resin functionality and appears to be a prerequisite for successful use of resins such as epoxies. In the following paragraphs various approaches using highly reactive resin systems for addressing this problem are discussed. A section is also included on the use of fillers to enhance further the properties of the cured resin.

#### Epoxy Resins

Selection of the appropriate epoxy resin and choice of curing agent from the myriad commercially available systems greatly complicates selection of the most desirable system. The curing agent must react at room temperature to form a useful glass, display optimum Case III characteristics, and afford an ultimate  $T_g$  greater than the maximum-use temperature. In addition, Case III characteristics can be markedly influenced by the addition of catalysts that accelerate the amine-epoxide reactions. A wide variety of these materials is available. There is also a question as to the effect of curing agent functionality. The prime candidates for repair matrices appear to be the cycloaliphatic amines and compounds of this type containing more than two primary amino

groups per molecule. However, these are not as readily available. This approach may well require synthesis of new curing agents. The latent proton-generating catalysts developed by Crivello (1980) may offer some potential for rapid polymerization of epoxies. Further details on specific materials for an epoxy resin program are given in Chapter 6.

Proprietary formulations should not be overlooked, and in-depth contacts with commercial sources should be made since there were indications that proprietary systems were available that may address these problems. However, the extensive effort expended on the epoxies to date without arriving at a solution to the problem of room-temperature curing indicates that a breakthrough would be difficult.

#### Acrylate Esters

The acrylate or vinyl esters, also referred to as the bis GMA resins\* or the epoxy acrylates, are produced from the reaction of acrylic or methacrylic acid with various epoxy resins. It is surprising that these products have not received more attention as candidates for composite field repairs. The literature on commercial products indicates that they cure rapidly and may have physical characteristics similar to epoxy adhesives.

A wide range of these products is available, since any epoxy resin can readily be converted to the vinyl ester. A variety of conventional vinyl monomers can be used as diluents for the purpose of obtaining wet lay-up characteristics. Since organic peroxides are the normal curing agents, redox systems can be developed that cure rapidly under subambient conditions. Further, by using a mixture of peroxides with different dissociation rates, it should be possible to match cure rates with external heating rates. The data in Table 1 show a comparison between bis GMA networks and Epon 828 cured at 160°C (320°F).

During the course of the study, committee member G. Wilkes carried out some studies that indicate a high probability of success for these materials. A 50-50 mixture of bis GMA and triethyleneglycol dimethacrylate (TEGDM) was cured for 24 hours at room temperature using a peroxide as catalyst. The dynamic mechanical properties were then measured while heating at 2°C/min (3.6°F/min). While the initial Tg of the polymer should have been about 60°C (140°F), the storage modulus curve, Figure 4, does not drop rapidly until 120°C (248°F). Thus the cure can be rapid enough that the Tg of these materials, with the proper mixture of catalysts, may keep pace with aerodynamic heating, at least up to 120°C (248°F). Further, the modulus data suggest that the resin could have useful matrix properties at least up to 175°C (347°F). Considering the number of acrylate esters and vinyl monomers available and the versatility of peroxide curing, this approach has considerable merit. In particular, certain tetrafunctional methacrylate esters have shown

\* The most common product is bis GMA itself, the dimethacrylate of the diglycidyl ether formed from bisphenol A.

TABLE 1 Bis GMA Networks With Three Modifiers  
(cured at 160°C (320°F) for 24 hours)

Sample	Modifier Percent (by Weight)	Modifier	Tg <sup>a</sup> (°C)	T <sub>p</sub> <sup>b</sup> (°C)	T <sub>j</sub> <sup>c</sup> (°C)
1	none	--	191	117,198	92,224
2	Styrene	10.5	189	112,183	--
3	2-Ethylhexyl acrylate	10.7	179	106,180	81,220
4	Vinyl-terminated disiloxane	10.9	179	89,184	78,213
5 <sup>d</sup>	Epon 828 + PACM-20 <sup>e</sup>	--	148	152	181

<sup>a</sup> Obtained by differential scanning calorimetry (DSC); heating rate 10°C/min (18°F/min).

<sup>b</sup> Inflection points in penetration curves.

<sup>c</sup> Inflection points in storage modulus-temperature curves.

<sup>d</sup> EPON 828/PACM-20 diamine control cured at 160°C (320°F) for 2.5 hours.

<sup>e</sup> Bis(4-aminocyclohexyl)methane

SOURCE: I. Yilgor et al. 1983.

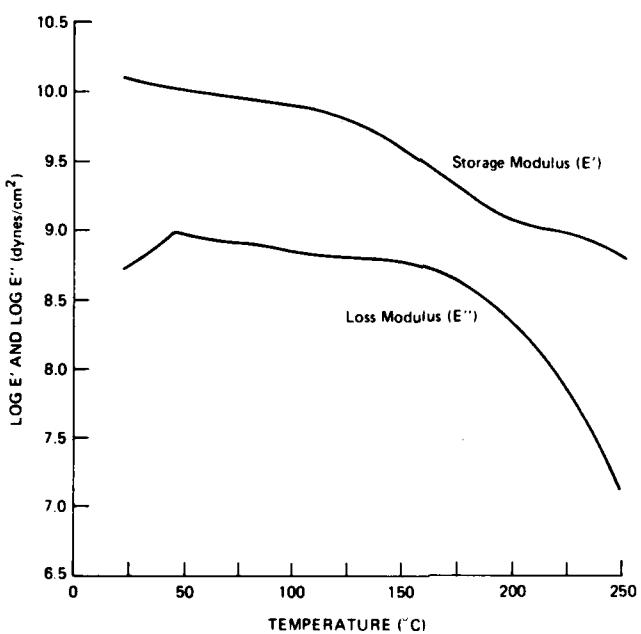


FIGURE 4 50/50 mixture of bis GMA and TEGDM aged 24 hours at 23°C (59°F); scan rate 2°C/min (3.6°F/min).

considerable promise as low-temperature-curable dental materials (Gebelein and Koblitz 1981). Further investigations in this area utilizing some of the recently developed rapid initiation techniques (to be discussed later) could lead to other fruitful results.

#### Rate Enhancement Approaches to Vinyl Polymers

In this section various concepts for enhancing rates of vinyl polymerization are considered, including rapid generation of radical initiators at low temperature, monomer design, and substituent effects.

The mechanism of radical-initiated vinyl polymerization is generally considered to consist of three steps: (a) initiation, which includes the high-energy process of generating a sufficient concentration of radicals; (b) the propagation step, the rate of which is predominantly related to the specific monomer system, and (c) the termination step, which is usually of low (or zero) energy requirement but depends largely on diffusion rates. Any change or modification that would favor steps (a) and/or (b) over (c) would result in higher cure rates. A variety of approaches to attainment of this goal are discussed here.

Several systems for rapid generation of radicals at low temperature have been developed within recent years (Lee et al. 1979; Minato and Furue 1974; Minato and Iwakawa 1974; Mishra 1981; Sugiyama et al. 1972). This approach would lower the energy requirement for the overall process, thus increasing the overall rate. Although much of the work directed toward the solution of the problem remains proprietary and unpublished, there appears to have been little or no effort to utilize this advanced technology in this area. A number of other parameters have recently been shown to affect the rate of radical-initiated vinyl polymerization. Among these are the polarity of the reaction medium (Plochocka 1981), complexation of the propagating radical by solvents (Kamanchi 1981), complexation of the monomer by a Lewis acid (Hirooka et al. 1968), increasing propagation rates via substituent effects (Odian 1981), and increasing propagation rates via complexation of an electron-donor monomer with an electron-acceptor monomer (Mulvaney et al. 1983; Shirota and Mikawa 1977). None of these techniques for increasing propagation rates of vinyl polymerization appears to have been investigated as a means of solving the problem at hand.

Substituent effects on the vinyl group may also be a significant factor in achieving the objective of low-temperature-curing systems. For example, vinyl acetate polymerizes about 15 times faster than styrene. Polymerization and/or copolymerization of suitably designed multifunctional vinyl monomers via initiators that provide suitable radical concentrations at low temperature could conceivably solve the problem of low-temperature curing of resin matrices.

A novel system for extremely rapid cross-linking or chain extension of certain divinyl compounds or prepolymers involves the "ene" reaction of these substances with N-substituted triazolinediones (N-phenyltriazolinedione is isoelectronic with N-phenylmaleimide) or bis-triazolinediones (Butler 1980). The reactions are complete within a

few seconds, and the prospects are excellent for development of an unusually rapid curing system, provided an appropriate two-component system having the necessary compatibilities can be devised.

#### Locally Ordered Charge-Transfer Systems

One of the most promising approaches for an intermediate-range study is the use of charge-transfer complexation between suitable pairs of vinyl monomers. Charge transfer complexes can be considered as locally ordered systems for free-radical polymerization. (Local ordering to promote reaction is discussed further in the section of this chapter on preordered reactions.) If an electron acceptor and donor are copolymerized, the rate of polymerization can be enhanced well over that expected for normal polymerization for two reasons: first, the cross-polymerization rates are high, since the molecules are of opposite polarity. Second, the complex (a combination of a donor and acceptor monomers) is extremely reactive, much more so than either monomer separately. In addition, two units are added in one reaction step when the complex is incorporated into the growing chain. In many cases there can be spontaneous cross-initiation, which means that little or no initiator need be used, and copolymerization often proceeds up to a hundred times faster than homopolymerization of either monomer alone.

During the course of this study, it was shown experimentally by committee member G. B. Butler, that copolymerization of m-tolylmaleimide with a bis-vinyl ether in a 2:1 molar ratio was initiated rapidly at 25°C (77°F) with a dimethylaniline-benzoyl peroxide system to give a solid copolymer, the internal temperature of the mixture rapidly rising to 75°C (170°F). Conceptually, this approach could be utilized as a rapid-curing matrix resin. For example, a suitable electron-donor monomer such as a bis-vinyl ether, preferably a liquid, containing one component of a suitable redox initiator, would constitute one component of a two-component system. A suitable electron-acceptor monomer--for example, a maleimide, maleate ester, fumarate ester, bis-maleimide, or low-molecular weight maleate or fumarate ester--being a liquid capable of contributing the necessary viscosity to the system and already containing the second component of the redox initiator, would constitute the second component of the two-part system. The system could be utilized by mixing the two components, which should produce a homogeneous liquid of suitable viscosity, followed by application to the structural fiber to produce the composite matrix. The system should be designed so that initiation occurs at ambient conditions within a reasonable time after mixing and lay-up. A variety of low-energy redox initiator systems are available. Examples of each of the required monomers are also known.

#### Novel Approach to Polymaleimide Matrices

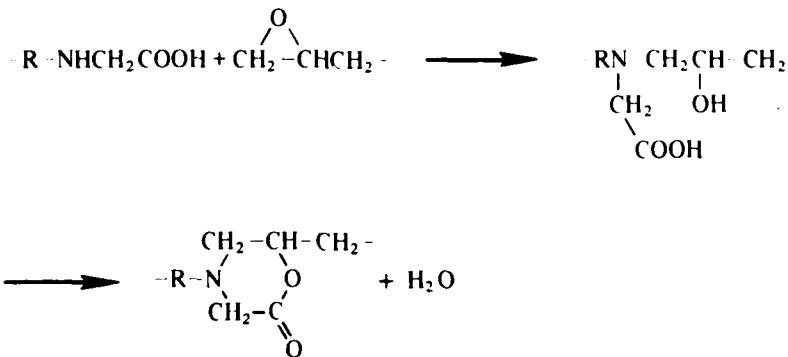
Bis-maleimides (Burns et al. 1970) and tris-maleimides (Vaughn and Buyny 1980) have been extensively investigated as thermally stable resin systems for composites. A novel approach to curing bis-maleimide systems could conceivably be based on the observations (Morita et al. 1981; Wagner-Jauregg and Ahmed 1974; Wagner-Jauregg et al. 1973; Yamashita et al. 1978) that imidazoles initiate trimerization of simple maleimides to

the corresponding hexa-substituted cyclohexane derivatives. Other vinyl monomers such as methyl methacrylate are also polymerized. Since some bis-and tris-maleimides are already commercially available, this mode of rapidly cross-linking such monomers could conceivably lead to low-temperature curing methods applicable to the current problem of field repair.

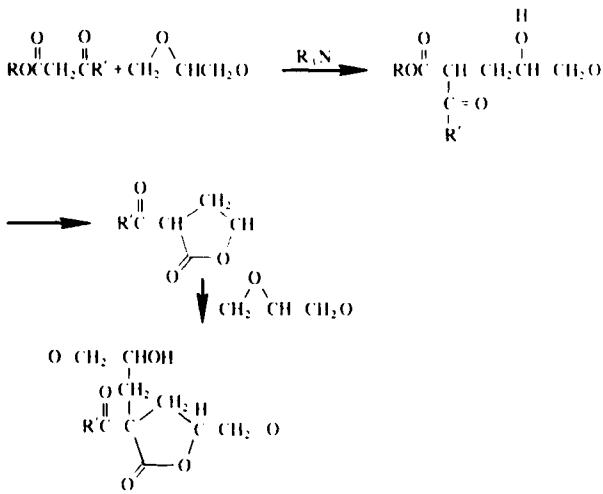
#### Intramolecular Processes

Problems with intramolecular cyclization were discussed in the previous chapter. The committee felt that some potential existed for further exploration of this approach. Thus, to address the earlier problems, a more flexible backbone or more reactive groups are needed. In addition, most cyclizations will generate small molecules, which is highly undesirable. However, since the matrix may absorb small amounts of water after it is made, the generation of several percent of water by-product during the cyclization could be tolerated. To some degree, the same criterion would apply to other small molecules released during cyclization. The following examples illustrate this approach:

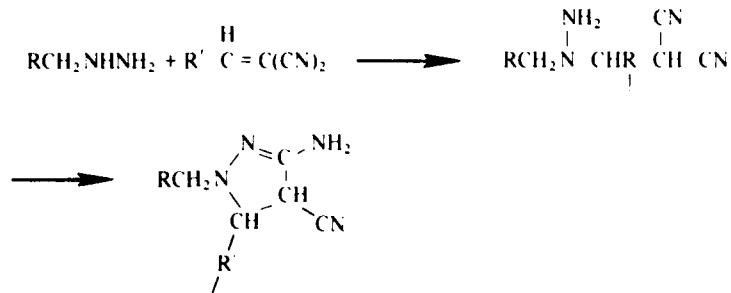
- o N-substituted glycines with epoxides (together with amine/epoxy reactions).



- o Epoxy-carbanion reactions (could be combined with epoxy-amine reactions).



- o Michael addition, using alkyl hydrazines as the nucleophile, with bis-cyanoacrylates and similar compounds.



#### Role of Filler

Use of fillers with the highly reactive systems described in this section may afford the incremental improvement necessary to meet the thermal requirements defined earlier. Thus, the committee feels that evaluation of fillers to enhance heat deflection temperature should be pursued with those systems that show the greatest promise. The specific areas that take priority for purposes of investigation are listed:

- o Effect of specific surface and filler content on solid-state thermal mechanical behavior, as well as the flow behavior of the uncured adhesive.
- o Influence of filler on resin-curing kinetics.
- o Relative wettability of the adhesive with a particulate filler and the potential of using coupling agents for obtaining better dispersability.

#### PREORDERED REACTIONS

There are severe difficulties to be overcome in considering the problem of getting a high-Tg polymer when polymerizing at room temperature. One unique approach to this problem suggested by the earlier work on polyimides is the concept of preordering.

Preordering can be accomplished by designing prepolymers in which the reactive groups are fixed adjacent to each other during the prepregging process. Reaction is then rapid because little or no molecular motion is needed for the groups to react. Here Tg has little relevance since there is little motion or diffusion of reacting groups.

Preordering of monomers has many precedents in solid-state and organized polymerizations. Acrylamide [mp = 85°C (185°F)] was found to polymerize at room temperature after it was irradiated to generate active centers (Morawetz 1966). Trioxane [mp = 64°C (147°F)] polymerizes very well to polyformaldehyde using cationic or X-ray initiation (Iguchi et al. 1969; Lando et al. 1962). More recently, many examples have been

found for the polymerization in the solid state of diacetylenes (Baughman 1972; Wegner 1969). Some will do so spontaneously at room temperature (Preziosi et al. 1983) with no initiator needed. In many cases the polymer is crystalline and retains the single-crystal nature of the monomer crystal (Baughman 1974; Day and Lando 1978). More recently other structures have been polymerized. One such monomer is p-phenylenediacrylic acid dimethyl ester [mp = 171°C (340°F)]. This can be photopolymerized at room temperature or below and, in fact, gives faster conversions and higher viscosities at lower temperatures (Hasegawa et al. 1981; Suzuki et al. 1969). Similarly, polymerization of p-acetoxybenzoic acid at 250°C (482°F) results in an ordered reaction yielding single crystals that do not melt at 500°C (930°F) [although there is a reversible transition at about 350°C (662°F)] (Economy et al. 1976).

Solid-state polymerization depends on the reactive groups being positioned so that the reaction to polymer can be accomplished with little or no change of the crystal dimension in the reaction direction. It can be very rapid. However, solid-state polymerization is not useful in this application since the monomer must be liquid so that it can flow, wet the fibers, and form a dense matrix.

The principle discussed here is documented, although less well so, for organized liquid systems. In particular, liquid crystal systems that order all molecules into planes, can be polymerized with large rate enhancements. Even simpler organizations can show this effect. For example, styrene sulfonic acid organized by salt formation with ionenes (cationic polymers) shows rate enhancement of 10<sup>3</sup> over homogeneous monomer solutions at the same concentration (Blumstein and Kakivaya 1977). Addition of ionenes has increased the rates of methacrylic and acrylic acid polymerization in solution (Tsuchida and Osada 1975). Similarly, and most important, monomers in the cholesteric and smectic state (and less so in the nematic state) tend to polymerize much faster than when in the isotropic state. Thus methacrylyloxybenzoic acid polymerizes 5 to 6 times faster in the liquid crystal state than in the isotropic state, and the polymer has 10 times the molecular weight of that from the isotropic polymerization (Konstantinov et al. 1967). Cholesteric liquid crystal monomers--e.g. cholesteryl methacrylate--polymerized about 50 times faster at 108°C (226°F) in the cholesteric state than at 120°C (248°F) in the isotropic state (Saki et al. 1972).

Difunctional vinyl monomers that exhibit liquid-crystal behavior have been synthesized and polymerized to cross-linked polymer (Strzelecki and Liebert 1973). The polymers still had the monomer liquid crystal organization.

A second approach, that of positioning reacting groups during the polymerization reaction, which subsequently react to form another polymer whose T<sub>g</sub> is significantly higher than the conversion temperature, is intriguing. Two specific examples are the cyclodehydration of polyhydrazides to poly-1,3,4-oxadiazoles (Frazer et al. 1964) and that of

polyamic acids to polyimides (Bower and Frost 1963). In all such cases, the groups that react to cyclize do not exist as such before the polymerization occurs. Two consecutive reactions occur: first polymerization, for which the Tg must be low (or solvent used), and subsequently the ring closure reaction, which can raise Tg.

#### Liquid Crystal Prepolymers

Liquid-crystal monomers and polymers have been the subject of intense study over the last few years (for example, Blumstein and Kakivaya 1977; Ciferri et al. 1982; Strzelecki and Liebert 1973). The major focus has been on the liquid-crystal temperature range and relaxation times of the polymers. However, liquid-crystal prepolymers have characteristics that could make them very useful as low-temperature-curing materials.

In the smectic liquid crystal form, molecules line up parallel with each other to form planar aggregates, but with rotational disorder. Such small-molecule liquid crystals are relatively nonviscous. The interaction of these two properties makes these monomers ideal for use in low-temperature-curing systems. Alternatively, viscous smectic oligomers can be designed that at relatively modest temperature convert to low-viscosity nematics, facilitating processing, and then on cooling would yield the more highly ordered smectics.

The advantage of the smectic and cholesteric liquid crystals over homogeneous systems is that all molecule ends are concentrated into a small fraction of the volume and are in contact with each other. If the polymerizing moieties are put at the ends of the molecules, they can react readily to high conversion. Here the concept of rising Tg stopping polymerization does not apply, since the reactive ends are positioned next to each other. Diffusion is not necessary for reaction to occur except at boundaries between ordered domains.

Several types of reactive centers can be used easily. Vinyl groups, especially acrylate and methacrylate esters, can easily be positioned at the ends of the molecules. They will react well by free-radical initiation.

A second system, which would show far less shrinkage during cure compared to the vinyls, consists of the low-temperature epoxy reagents, epoxy (perhaps glycidyl ethers) with amines. This is a more difficult system to manage, since the two monomers must be mixed before use and must reform a mixed liquid crystal before reaction.

There are many other possible systems; the only restrictions are these:

1. The reaction should proceed reasonably rapidly at ambient temperature.
2. The reactive moiety can be put at the ends, middle, or on the side chains of a liquid-crystal-forming molecule but in all cases has to react by an addition polymerization process.

3. The liquid crystal can either be a monomeric smectic at room temperature with the desired viscosity or an oligomeric smectic that converts to a nematic 10 to 20°C (18 to 36°F) above ambient temperature.

## NOVEL CURING TECHNIQUES

As indicated in the background section, there is a fundamental barrier to achieving elevated-temperature properties in conventional resin systems cured at ambient temperature. At the same time, field conditions often preclude access to the rather cumbersome equipment needed for elevated-temperature curing. In this section, consideration is given to novel alternative curing techniques. Although these approaches each involve some hardware, it is, in principle, less complex than that required for external heating.

### Electroinitiation of Matrix Resin Polymerization

The use of graphite fibers as electrodes for the electroinitiation of polymerization has been described in some detail, especially by Phillips et al. (1977) and Subramanian and Jakubowski (1978). Both of these reports dealt with dilute solutions of monomers that also contained substantial concentrations of support electrolytes. The cathode and anode were isolated from one another by means of a glass frit between the cells. Polymers were formed, both anodically and cathodically, from a variety of monomers. In Subramanian and Jakubowski's work, grafting as well as plating onto the fibers was observed. Clearly, it is possible to form polymers utilizing graphite fibers as electrodes.

These results, of course, raise the possibility of using the graphite fiber reinforcements in a patch as electrodes for cure initiation. Unfortunately, for several reasons, this most attractive possibility does not appear practicable. First, the apparent need for a support electrolyte probably could not be tolerated in a composite where the ionic activity would severely degrade its environmental durability. Second, it would be necessary to incorporate both the anode and the cathode into the patch. In a thin section, it would be extremely difficult to keep them separate, especially under the external pressure likely to be required during patch application. Finally, as polymerization proceeded, it is likely that polymer coatings would form around the fibers, effectively insulating them and thus preventing further electric activity. For these reasons, it is concluded that electroinitiation from graphite fibers is not feasible for the curing of composite patches.

### Waveguide Curing

Ultraviolet/Visible Optical Fibers for the Initiation of Resin Cure. Optical fibers useful in the ultraviolet (UV)/visible region of the spectrum constitute a well-developed technology and are readily available. The suggested approach would be to incorporate optical fibers

for photoinitiation of the resin cure into a composite structure; the fibers would remain in the part or repair patch after processing. A cursory screening of the literature revealed no examples of their use for in situ photoinitiation of chemical reactions, although their use in small, hand-held devices to concentrate UV light onto UV-curable dental fillings based on vinyl esters has been indicated.

There does not appear to be any fundamental barrier to the use of such fibers for the photoinitiation of resin cure in composite patches. The epoxy resins cured by cationic photoinitiation as reported by Crivello and Lam (1977) and Schlesinger (1974) would be prime candidates as matrix resins for graphite fiber composite patches curable by UV/visible radiation, as would systems based on vinyl esters, which appear attractive for several other reasons. Ultimately, the photoinitiation of a hot-reaction matrix resin by this technique could be addressed. In fact, this may be an advantageous combination, since it can circumvent one of the principal drawbacks to the hot-reaction approach--i.e., incomplete and/or nonuniform curing caused by quenching from the heat-sink effect of the structure being repaired. The evenly distributed optical fibers would initiate cure instantaneously and uniformly throughout the repair, thereby minimizing heat transfer. In addition, photoinitiation has the advantage of utilizing a one-part system, thus avoiding problems of stoichiometric imbalance and incomplete mixing of components.

Major issues to be addressed in pursuing this approach are the number and distribution of optical fibers in the patch. It is envisioned that the optical fibers would be incorporated along with the reinforcing fibers during the fabrication of prepregged patch material. What are unknown are the distribution of fibers required to effect complete cure of the matrix and the design of optical fibers with controlled light leakage to ensure optimal illumination. Variation of the index of refraction and incorporation of a varying defect concentration along the fiber are possible approaches. An additional issue is the effect of such fibers on the mechanical properties of the cured patch. Too many fibers would obviously degrade these properties.

Infrared (IR) Optical Fibers as a Selective Heat Source for Resin Cure. Whereas UV/visible optical fibers constitute a well-developed technology, IR optical fibers are just beginning to emerge from the laboratory and become commercially available. Indeed, the best of them, based on heavy metal fluoride glasses (Drexhage et al. 1980), must still be regarded as research materials and are thus at this point extremely costly. Other, less expensive fibers based on polycrystalline materials such as KRS-5 (thallium bromide) or chalcogenide glasses such as  $\text{As}_2\text{S}_3$  are more readily available. Each has disadvantages, however. The former are quite brittle, and both are rather "lossy" in terms of their transmittance. Still, they may be useful for thermally polymerizing patch matrix resin, since only a few meters of fiber would be required. The heavy metal fluoride glasses such as  $\text{ZrF}_4\text{-HfF}_4\text{-BaF}_2\text{-ThF}_4$  have very high transmittances and would be

the materials of choice when their cost and availability permit. The major advantage of this approach is, of course, that it is an alternative means of thermal curing. Thus it can be used with conventional epoxy resin systems and probably will not require new resin development. As with the UV/visible optical fibers, the crucial issue is the number and distribution of fibers required to achieve complete resin cure.

#### Photocuring of Adhesive Bond Lines

Whereas the preceding approaches have dealt with the curing of matrix resins in uncured composite patches, this section is concerned with the photochemical curing of adhesives for the attachment of fully cured patches.

Two approaches appear worth investigating. In the first, the bond line itself could act as a waveguide. Here, light from an appropriate source would be directed onto the edge of the bond line. Given the appropriate refractive index of the adhesive, the light would undergo multiple internal refractions and so penetrate the full width of the bond, thus effecting cure. The problem to be addressed is the development of adhesives having the requisite optical properties.

The second approach is a variant of the use of UV/visible optical fibers for matrix resin cure. In this case, the optical fibers would be perpendicular to the plane of the patch, at least in the area of the bond line. Thus situated, they provide light access to the bond line thereby permitting the use of UV-curable adhesives. Once again, the critical issue to be addressed is the distribution of fibers needed to effect complete cure.

In summary, novel curing techniques that were considered are (a) inductive heating, (b) microwave heating, (c) ultrasonics, (d) UV and visible radiation, (e) high-energy radiation, (f) electron beams, and (g) electroinitiation. With the exception of the use of appropriate radiation energy (e.g., UV or IR) with appropriate waveguides (optical fibers) embedded in the matrix as curing techniques via latent catalysts, the equipment required for these novel methods is considered too cumbersome, too expensive, too impractical, and/or too complicated for use under the necessary field conditions. There appear to be several promising approaches to composite field repair based on waveguide curing techniques. A proposed program for the exploration of these approaches is given in Chapter 6.

Interestingly, during the final stages of the committee's work, a U.S. patent (4,385,957) was issued that dealt with laminate cure by resistance heating of carbon fibers. This concept should be tested to determine the suitability of the technique for field repair.

#### OTHER APPROACHES USING LOW T<sub>G</sub> SYSTEMS

Because the modulus requirements for an adhesive are lower than those for a matrix, a greater latitude in approaches to the former is

permissible. It is clear that when the temperature is raised through the T<sub>g</sub> the modulus of a polymer drops drastically. A number of modifications to the adhesive, however, will raise the high temperature end of the modulus/temperature curve, even though the T<sub>g</sub> will scarcely be affected. These include, for example, cross-linking, crystallization, and the use of fillers. This is illustrated schematically in Figure 5. The point is that, even though the temperature is above the T<sub>g</sub>, with suitable modification the modulus may be high enough to be above the required minimum for an adhesive. Thus, in principle, it is possible to operate with an adhesive that has a T<sub>g</sub> at or close to room temperature but has acceptable physical properties at the higher temperatures caused by aerodynamic heating.

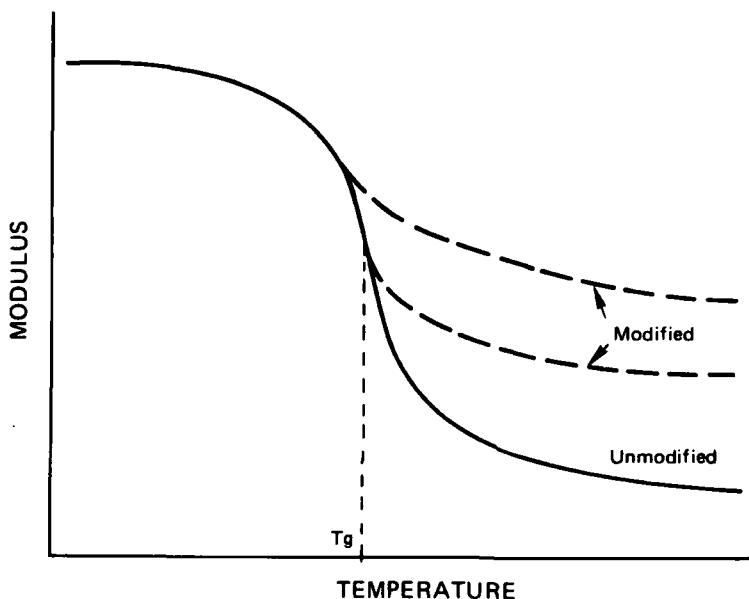


FIGURE 5 Schematic modulus-temperature curves for modified and unmodified adhesive resins.

In another illustration, there is at least one aircraft adhesive consisting of a butadiene-acrylonitrile rubber reinforced with a phenolic resin (J. Quinlivan, private communication). Although in this system, the phenolic resin requires curing well above room temperature, this illustration points to the possibility of a low-T<sub>g</sub> continuous phase whose modulus is raised to an acceptable level by modification.

Several approaches for achieving a high-modulus, low-T<sub>g</sub> system at relatively low temperatures are described in the following.

#### Phase Changes

Crystallization. An effective way to gain substantial increases in modulus involves crystallizing amorphous polymers. Increases in modulus of up to 2 orders of magnitude have been observed. For example, Stevenson (1983) observed a 200-fold increase in modulus on crystallizing

natural rubber. He suggested that the crystallites formed an interconnecting network that stiffened the rubber comparable to that of a fiber composite structure. Mohajer and Wilkes (1982), studying copolymers of lactic and glycolic acids in film form above their Tg, found a marked change of modulus as spherulite content changed, which could be explained by a simple composite model.

The major problem is to develop a method that would induce rapid crystallization at room temperature in an amorphous, adhesive polymer film, while keeping the film from crystallizing under storage conditions. This requires either heating the film once it is placed in the glue line (not acceptable) or adding solvent to plasticize the film and aid crystallization. Since the solvent cannot diffuse out easily, this approach is fraught with difficulties.

Given these considerations, the crystallization approach is considered to have a low probability of success.

Phase Inversion. Another approach to raising the modulus at ambient temperature is via polymer phase inversion. A dispersion of a high-Tg, high-modulus polymer in a low-Tg polymer matrix could be laid down as the adhesive layer. After mating the surfaces, a solvent would be introduced along the periphery that favors inversion of the dispersion so that the high-Tg component now becomes the continuous phase. Such a dispersion would probably be close to 50 percent by volume in each component. Phase inversions are common in small-molecule dispersions where, for example, oil-in-water emulsions can be inverted to water-in-oil and vice versa. Films of block copolymers, consisting of incompatible blocks, demonstrate inverted phases when the solvents from which they are cast thermodynamically favor one block over the other.

Potential problems such as penetration of the solvent, incomplete fusion of the high-Tg continuous phase, and the removal of the solvent are apparent in this approach, and it too is considered to have a low probability of success.

#### Reactive Solvents and Plasticizers

This approach envisages a solution or perhaps a swollen dispersion of a high-Tg, high-modulus thermoplastic in a solvent that is itself polymerizable. For adequate shelf life, the formulation is compounded with a room-temperature curing system that probably consists of two parts. The mixture is fluid enough to wet adequately the working surfaces. After mating of the parts, polymerization proceeds, creating a polymer blend in situ. Grafting onto the high-Tg polymer would create a more homogeneous blend with smaller domains.

For this approach to work, the resulting blend or the graft polymer parts should be thermodynamically incompatible; the final cured adhesive line would demonstrate two glass transitions, one at high temperature (from the starting thermoplastic) and one at low temperature (from the polymer or graft derived from the reactive solvent). The utility,

however, would reside in a favorable ratio of the two components. If enough of the high-modulus polymer is present, the composite modulus could be high enough to more than compensate for the presence of the low-Tg material. This system has the very important advantage that solvent need not be removed.

Among the thermoplastics potentially useful in this approach are a variety of engineering polymers that are commercially available. These should not be so intractible that there are few solvents for them. Given an intractible polymer to start with, the odds of finding a polymerizable solvent, let alone a simple solvent, would be very low. Polymers that are both high-modulus and are reported to be readily soluble in a number of common solvents include polysulfones and poly(phenylene oxide).

Suitable monomers should include acrylates and methacrylates, preferably cross-linkable, such as the di, tri and tetra varieties. These would contribute to rapid polymerization (setting) of the adhesive and offer potential for higher modulus than simple monoacrylates or methacrylates.

In summary, the reactive plasticizer and solvent system described appears to have potential and should be pursued.

## 6. RECOMMENDATIONS

This chapter contains the committee's recommendations for research and development areas to be pursued by the Department of Defense. They are divided into near-term and longer term programs and have been ranked by the committee as Outstanding, Excellent, or Good. These judgments are based on a number of considerations including the availability of materials, precedents for the proposed physical and chemical concepts, and probability of success. In the case of highly reactive systems further cure can take place during the measurement of Tg. A rapid, concise screening procedure to determine Tg unambiguously will be needed to sort out the prime candidates. The following research and development areas are recommended:

<u>Topic</u>	<u>Ranking</u>	<u>Program Period</u>
Acrylate esters	Outstanding	Near-term
Preordered Reactions	Outstanding	Longer term
Epoxy resins	Excellent	Near-term
Donor-acceptor complexes	Excellent	Longer term
Fillers	Excellent	Near-term
Waveguide curing	Excellent	Near-term
Reactive solvents	Excellent	Near-term
Secondary ring closing reactions	Good	Longer term

Descriptions of the recommended approaches are provided in the following sections of this chapter. Further details are given in the appropriate sections of Chapter 5.

### NEAR-TERM PROGRAM (1-3 YEARS)

#### Acrylate Esters

The basic molecules to be studied consist of the dimethacrylates and diacrylates of conventional epoxy resins. A typical product is the dimethacrylate of the diglycidyl ether formed from bisphenol A (bis GMA). The commercial producers of acrylate esters should be encouraged to supply materials or information early in the program. The basic molecules should be formulated into wet lay-up laminating resins using low-molecular-weight vinyl derivatives such as styrene, acrylate esters, glycol methacrylates, or diallyl phthalate. There are also a number of cycloaliphatic diepoxides commercially available that can be readily converted to acrylate or methacrylate esters. The choice of the diluents is important to this effort since it can influence the magnitude of the increase of Tg over T<sub>cure</sub>.

In summary, these monomers are commercially available, easy to study, fast-reacting systems and are probably better than the epoxies (Outstanding).

#### Reactive Solvents

Research should be pursued to develop systems based on high-Tg, high-modulus thermoplastics dissolved or dispersed in highly reactive solvent-initiator combinations. Such systems might well include tri- and tetramethacrylate solvents that by themselves rapidly polymerize free-radically to highly cross-linked polymers. Initiators would be of the redox type. Shelf-life considerations, of course, would preclude one-package systems.

Suggested plastics include the engineering resins--e.g., polyetheretherketone (PEEK), polysulfones, polycarbonate, polyarylates, and poly(phenylene oxide). Some suggested reactive solvents are glyceryl trimethacrylate, pentaerythritol tetramethacrylate, polyethyleneglycol dimethacrylates, ethoxylated glycerine trimethacrylates, ethoxylated pentaerythritol methacrylates, and divinylbenzene. Redox initiator systems may include peroxide-aromatic amines, peroxide-sulfinites, and peroxide-metal naphthenates.

The feasibility of this approach should be demonstrated over a 2- to 3-year period (Excellent).

#### Waveguide Curing

It is recommended that the several aspects of waveguide curing be vigorously pursued in a phased program. Because of fiber availability, approaches based on UV/visible optical fibers should be pursued in the near- to mid-term, while research based on IR fibers could be considered in the longer term.

Key questions related to UV/visible optical fibers include the means for taking light from the fibers (e.g., by a series of breaks in refractive coating or by point sources at the fiber ends only); the distribution of fibers required for complete cure; the potential of using fillers or voids to disperse the light; and the effect of fibers on mechanical properties and durability. These questions should be resolved using a standardized photo-curable epoxy.

To a large extent, the sequence of activities outlined for UV/visible fibers is directly applicable to IR fibers, although the latter are yet to be optimized. Thermally cured resin systems, probably conventional epoxies, would be substituted for photo-curable resins. Thermally initiated vinyl ester systems could also be included.

In summary, the fibers are available and there is no reason why the concept should not work (Excellent).

### Epoxy Resins

Epoxy resins with more than two functional groups should be a prime consideration. Since most of these resins are solids or semisolids, formulation with resins of lower viscosity will be required to obtain viscosities suitable for wet lay-up lamination. Examples of the latter are resorcinol diglycidyl ether, cycloaliphatic epoxides, and the diglycidyl ether of bisphenol A.

The choice of curing agent is more complex. The cycloaliphatic amines and imidazoles offer the most promise. Admixtures with aromatic amines should also be considered. The role of the accelerator is critical, but selection is complicated by the wide variety of systems available.

In summary, these materials are commercially available and are currently used as matrices in composites. Further work is needed to exploit current vendor activities (Excellent).

### Fillers

There appears to be a strong potential for utilizing a rigid filler for enhancing the mechanical properties of both the adhesive and matrix layer and for increasing the ultimate-use temperature. The specific areas that should be investigated are (a) the effect of specific surface and filler content on solid-state thermal mechanical behavior as well as the flow behavior of the uncured adhesive; (b) the influence of the filler on resin curing kinetics; and (c) the relative wettability of the prepolymer with a particulate filler and the potential of using coupling agents as a means of obtaining better dispersions.

This study should be carried out in conjunction with those focused on the development of new or modified matrices.

The concept of using fillers is applicable to many of the recommendations presented here. Filler can enhance the modulus retention of the adhesive or matrix resin and provide an important approach for further improving the properties of systems such as acrylates and epoxies (Excellent).

### LONGER TERM PROGRAM (3-5 YEARS)

#### Preordered Reactions

Liquid-crystal prepolymers that incorporate reactive groups are suggested in this section. Experiments have shown that lower melting smectic liquid-crystalline material can be made if flexible spacers are included. For example, if an aromatic nucleus is used and flexible groups are attached at each end, one can usually generate a smectic liquid-crystal form.

Variation of the flexible spacer and the length and nature of the aromatic core will vary the liquid temperature range. Suitable materials

can be found that show smectic-nematic transitions at 40-50°C (104-122°F). The nematic would provide the necessary flow and the smectic the desired ordering. Alternatively, very-low-molecular-weight smectics may display sufficient flow to permit processing.

There are several polymerization reactions that can be easily adapted to the liquid-crystal approach. Vinyl groups can be added in the appropriate positions using methacrylate or acrylate esters, although many other monomers can be used. Other reactive groups, such as epoxies and epoxy-amine systems, could also be used.

The very high local concentration of reactive groups in the smectic phase implies that reactions will occur more rapidly than in an isotropic medium and affords a novel solution for overcoming the theoretical barrier toward producing a resin with a Tg higher than the cure temperature.

In summary, this approach offers a good opportunity to produce polymers at room temperature that would be rigid at high temperatures (Outstanding).

#### Secondary Ring Closing Reactions

Many of the potential reactions have been well studied and therefore are easy to adapt to this purpose. Some are well known in the industry, such as reactions using di- and triglycidyl ethers and polyamines. A disadvantage is that, in many reactions, small molecules are produced. Also, the primary polymerization reaction must be much faster than the secondary cyclization; otherwise the Tg will rise too early and prevent the polymerization from reaching completion.

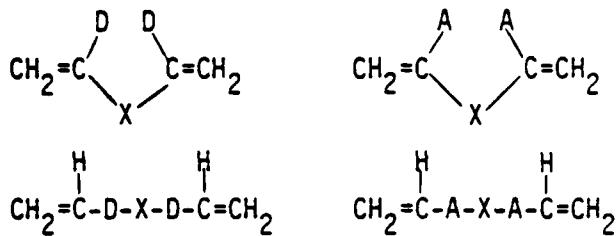
The simplest approach is to use known epoxy monomers that can react with analogs of known molecules. Such a possibility could be the partial replacement of amines with substituted glycines that would cyclize to lactones. Also, carbanions could be utilized; such materials could be analogs of malonic esters or cyanoacetic esters and could react with epoxies. These would cyclize to lactones or imino ethers. The advantage of these monomers is that they are nonviscous liquids and could be used as reactive diluents in combination with amines.

In summary, there is precedent for such secondary reactions raising Tg well above the reaction temperature. However, there are potential problems to be coped with because of the production of small molecules and the timing of the primary and secondary reactions (Good).

#### Donor-Acceptor Complexes

Copolymerization of certain vinyl monomer pairs occurs under the influence of appropriate initiators up to 100 times faster than homopolymerization of either monomer. This enhanced rate has been attributed to lowering of the activation energy for initiation and propagation, both of which occur in a donor-acceptor complex (DA) between the monomers rather than on the individual monomers. Such systems lead

to steric control in the resulting copolymer as well. It is suggested that an intermediate-range research program be initiated to investigate the potential for solving the problem of room-temperature-curing resin systems. Monomer pairs that meet the basic requirements for such a DA preordered matrix can be generically illustrated as follows:



where D = a monovalent or divalent donor atom or group; A = a monovalent or divalent acceptor atom or group; and X = a divalent connecting group.

Initiation could be spontaneous; however, if not, initiation should be rapid at room temperature via use of novel initiating systems and/or additional structural modification.

Although a number of monomers for investigation are presently available, additional synthetic effort would be necessary to provide monomer pairs having optimum properties. However, such monomer pairs, based on known chemistry, are potentially inexpensive and such a system would compare in cost to present technology (Excellent).

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APPENDIX  
BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

JAMES ECONOMY received a B.S. degree from Wayne State University and a Ph.D. in chemistry from the University of Maryland. Since graduation he has been employed by the University of Illinois, Semet-Solvay Petrochemical Division of Allied Chemical Corporation, and Carborundum Corporation. Presently he is employed by IBM Corporation, San Jose. His research interests include high-temperature polymers, thermosetting and photoconductive polymers, ceramic and organic composites, and flame-resistant polymers.

GEORGE B. BUTLER received a B.A. degree from Mississippi College and a Ph.D. in chemistry from the University of North Carolina. He was employed with Rohm and Haas Company before becoming a professor of chemistry at the University of Florida. His research interests include resins and plastics, pharmaceuticals, and polymerization mechanisms.

NATHAN D. FIELD received a B.S. degree from City College of New York, an A.M. from Columbia University, and a Ph.D. in polymer chemistry from the Polytechnic Institute of Brooklyn. He has been employed by E. I. du Pont de Nemours, Inc., Atlantic Refining Company, GAF Corporation, International Playtex Company, and Dart Industries. Presently he is a professor of chemistry at The City College of the City University of New York. His research interests include polymer blends, water-soluble polymers, and organic synthesis.

JOHN K. GILLHAM received B.A. and M.A. degrees from Cambridge University and a Ph.D. in chemistry from McGill University. After graduation he was employed by the American Cyanamid Company. Presently he is a professor of chemical engineering at Princeton University. His research interests include molecular structure and temperature-dependent properties of polymeric materials, polymer synthesis, and polymer degradation.

MORTON H. LITT received a B.S. degree from City College of New York and a Ph.D. in polymer chemistry from the Polytechnic Institute of Brooklyn. After a fellowship at Manchester University, he was employed by Syracuse University and Allied Chemical Corporation before becoming a professor of polymer science at Case Western Reserve University. His research interests include ionic and free-radical polymerization mechanisms, polymer mechanical and electrical properties, and organo-fluorine chemistry.

CLAYTON MAY received a B.S. degree in chemistry from the University of California, Berkeley, and a B.S. in engineering from New York University. After employment with Shell Development Company, he moved to his present position with Lockheed Missiles and Space Company, Inc. His research interests include polymer chemistry, particularly thermosetting resins, epoxides, and the development of vinyl ester resins.

JOHN T. QUINLIVAN received a B.S. degree from Gonzaga University and M.A. and Ph.D. degrees in chemistry from Princeton University. After graduation he was employed by the University of California, San Francisco. His present position is with the Boeing Company. His research interests include physical properties of macromolecules, failure mechanisms of fiber-reinforced polymers, and composite materials.

GARTH L. WILKES received a B.S. degree from the State University of New York, College of Environmental Science and Forestry, and M.S. and Ph.D. degrees from the University of Massachusetts in physical chemistry. After graduation he became a professor of chemical engineering at Princeton University. Presently he is a chair professor of chemical engineering at the Virginia Polytechnic Institute and State University. His research interests include the structure-property behavior of synthetic polymers and biopolymers.

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